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HEAVY METALS AND THE PETROLEUM INDUSTRY

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KATHERINE DANIELS WARE, B.S.

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REPORT

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ABSTRACT

The purpose of this report is to investigate the amounts of heavy metals introduced into the environment by the petroleum industry during exploration and production operations, to examine their environmental impacts, and to compare those impacts to the heavy metals production from natural and other man-made sources. Heavy metals are of concern because they can impact the health of living organisms that they contact.

The petroleum industry contributes only a small fraction of the heavy metals to the environment compared to both natural sources and other industrial sources of heavy metals. The bioavailability of the metals introduced into the environment by the petroleum industry are very low. Recycling and proper waste treatment and disposal are viable options for reducing the environmental impacts from heavy metals. Methods successfully tested in the field include stabilization and solidification, recycling of treated produced water, drilling fluids, drill cuttings and oily sand wastes. The relatively small amounts of metals

introduced into the environment by the petroleum industry, the low bioavailability of these metals, and the availability of effective waste treatment methods, translates into a minimal impact from metals on the environment by drilling and production operations. Heavy metals from the production of petroleum, properly handled, are not a threat the environment.

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CHAPTER 1. INTRODUCTION

The purpose of this report is to investigate the amounts of heavy metals introduced into the environment by the petroleum industry during exploration and production operations, to examine their environmental impacts, and to compare those impacts to the heavy metals production from natural and other man-made sources. The transport and interactions of the heavy metals with soil are also reviewed.

Metals are a distinct group of elements and are the most abundant of the elements. The term 'heavy metals' is used to describe toxic metals with a specific gravity greater than four. A metal can be termed toxic when a living organism is exposed to some concentration of the metal and adverse effects are noted. A more exact term is "toxic metals and metalloids," since they include the light metal beryllium and metalloids arsenic and selenium.¹ The terms heavy metals, toxic metals, trace metals, and metals are often used synonymously. The metals most commonly monitored in the environment are cadmium, chromium, copper, iron, lead, manganese, mercury,

nickel, and zinc. These metals are monitored because they are very common in the discharge of industrial processes and are very toxic.²

Since the industrial revolution began, huge changes in the location and concentration of metals in the environment have taken place. Because metals are naturally occurring, it is the increasing concentrations of metals that are of concern. Chapter 2 discusses man-made and natural sources of heavy metals. Heavy metals introduced into the environment from the petroleum industry are discussed in Chapter 3. Chapter 4 discusses how metals are transported in the environment and what interactions occur between the metals, soil, and water. The characteristics of the metals and their potential toxicity is described in Chapter 5. To prevent environmental impacts from occurring, the heavy metals must be managed. The methods available for managing metals wastes, including containment and cleanup, are discussed in Chapter 6.

CHAPTER 2. SOURCES OF HEAVY METALS

Heavy metals are discharged into the environment through many sources. These sources include: geologic weathering, catastrophic geologic events, industrial processing of ores and metals, use of metals and metal components, leaching of metals from garbage and solid waste disposal sites, storm water runoff, and animal excretions.³ The pre-civilization concentrations are based on geologic weathering and natural occurrence. In some locations, metals naturally occur in toxic concentrations. With the rise of civilization, the concentrations of heavy metals have risen in urban areas relative to remote or pristine areas. These higher concentrations of heavy metals threaten the environment.

Metals are introduced into the environment through two categories of releases: point sources and non-point sources. A point source pollutant is a discharge from a specific activity with an identifiable discharge point, such as cooling tower discharge or water treatment plant effluent. Non-point sources are uncontrolled pathways such as surface drainage and atmospheric

deposition.²

2.1 NATURAL SOURCES OF HEAVY METALS

Heavy metals are naturally occurring and can be transported through the environment by natural processes. Wind and water erosion cause naturally occurring heavy metals to enter the environment. Table 2.1 lists the average concentrations of the metals common in the geosphere and hydrosphere. Table 2.2 lists the elemental composition of native soils from an oilfield. The average concentration of metals in both tables are similar. Another major concentrated release of metals is through volcanic eruptions. Table 2.3 lists average yearly emissions of volcanic dust and gases and for wind blown dust from erosion.

2.2 MAN-MADE SOURCES OF HEAVY METALS

Surface drainage is a major man-made non-point source of heavy metals. Surface drainage consists of: agricultural runoff, urban runoff; road runoff, sewer infiltrations, deicing; solid waste leachate, and sludge disposal; industrial runoff from mining

tailings; and subsurface leaching.² In the Great Lakes, 85-99% of lead is from non-point sources, and a primary source of the lead is from leaded gasoline. Lead in gasoline has been the largest single source of air pollution.² Leaded gasoline is currently prohibited in for use in vehicles in many areas. The amount of lead from non-point sources has decreased with the increased use of unleaded gasolines.⁵

The primary man-made point sources of metals are from industrial waste streams. Because the source is identifiable and can easily be contained and monitored these sources of metals are generally restricted according to applicable regulations.

In industrialized areas the magnitude of wastewater and atmospheric sources are about equal. For example, a Lake Erie inventory revealed man-made atmospheric inputs of copper, zinc and lead were 20%, 35%, 50% of the total amount of each metal present; while sewage effluent contributions were 45%, 30%, and 20% of the total.⁴

2.2.1 DOMESTIC SOURCES OF HEAVY METALS: Domestic

sources of heavy metals include solid waste disposal of cadmium and lead batteries, metal cans and structures, lead based paints, domestic solid sewage, used engine oils, combustion products from automobiles, leachate from domestic waste disposal sites, and storm water runoff.

Waste waters constitute the largest single source of increased metals concentrations in surface bodies of water. Table 2.4 contains average input rates of metals into the environment for several categories of land use. The table entries are listed in order of population density. From this table it can be seen that the rate of metal influx is dependent on the human population of the area.

2.2.2 INDUSTRIAL SOURCES OF HEAVY METALS:

Industries use a variety of metals and these metals are often released in their wastes. Table 2.5 lists a number of industries and the heavy metals which they use. The largest sources of metal wastes are from mining and metal processing.

Mine wastes are a large concern because of the immense quantities of ore required to obtain the desired metals. For example, the typical percentage of precious metal in ore is less than 0.5%. To produce one ounce of gold, 420 tons of ore must be mined.⁶ The leaching of unrecovered metals in the ore is increased because of the increased surface area available for reaction due to the crushed state of the ore. In addition, any metals in the ore with a low vapor pressure, e.g. mercury, are often vaporized during the smelting process.

Metal cycling is described as the time required for a metal to be removed from the ground by natural processes and subsequently returned. A short cycle represents a period in which the heavy metals are rapidly being released into the environment. Table 2.6 classifies some of the metals in a ratio of cycling time due to mining relative to natural cycling. Ratios of >10 are potentially hazardous to human health and the environment.⁵

Most industrial operations use metals in their daily operations. An investigation of New York City

wastewater in 1974 found that heavy metals are often introduced from a variety of sources. The average concentrations of metals in waste discharges from these industrial activities are listed in Table 2.7.

The concentrations of the metals released directly into the environment from industrial operations are more regulated today than in the past. In the U.S., industries are required to obtain a permit for discharges to water or air. The permitting requirements have reduced the flow of heavy metals into local sewage systems.

Another industrial source of heavy metals is atmospheric emissions. Metals enter the atmosphere as a vapor and as particulates through combustion of fossil fuels, cement production, and extractive metallurgy. Table 2.8 lists average air emissions from the industrial activities and combustion of fossil fuels (coal, oil, natural gas). Table 2.9 compares the metal emissions from the combustion of specific fossil fuels and the production of cement.

2.3 COMPARISON OF NATURAL SOURCES TO MAN-MADE SOURCES

The total amounts of heavy metals introduced to the environment by man-made sources is significantly greater than the amounts that are introduced through natural sources. Comparing Tables 2.3, 2.8, and 2.9, the quantities of most toxic metals released through industrial activities are several orders of magnitude greater than from natural sources. This increase in heavy metals from man-made sources can impact the environment.

TABLE 2.1: BACKGROUND CONCENTRATIONS AND GEOCHEMICAL MOBILITY
OF HEAVY METALS IN THE GEOSPHERE AND HYDROSPHERE²

ELEMENT	MEAN CRUST mg/kg	MEAN SOIL RANGE mg/kg	FRESHWATER RANGE ug/l	SEAWATER RANGE ug/l	GEOCHEMICAL MOBILITY
Antimony	0.2	0.2-10	0.01-5	0.18-5.6	high
Arsenic	1.5	0.1-40	0.2-230	0.5-3.7	very high
Cadmium	0.11	0.01-2	0.01-3	<0.01-9.4	low
Chromium(+3)	100	5-1500	0.1-6	0.2-50	very low
Chromium(+6)	----	-----	-----	-----	very high
Copper	50	2-250	0.2-30	0.05-12	low
Iron	4.18	4-558	10-1500	0.03-70	low
Lead	14	2-300	0.06-120	0.03-13	low
Mercury	0.05	0.01-0.5	0.0001-2.8	0.01-0.22	very low
Manganese	950	20-10000	0.2-130	0.03-21	very low
Molybdenum	1.5	0.1-40	0.03-10	4-10	high
Nickel	80	2-750	0.02-27	0.13-43	high
Selenium	0.05	0.01-2	0.02-1	0.052-0.2	moderate
Silver	0.07	0.01-8	0.01-3.5	0.03-2.7	high
Zinc	75	1-900	0.2-100	0.2-48	high

**TABLE 2.2: SUMMARY OF ELEMENTAL CONCENTRATIONS IN
NATIVE SOILS. (Alaskan North Slope) (mg/kg dry)^{1a}**

ELEMENT	MEAN	MAXIMUM	MINIMUM
Aluminum	7050.0	43800.0	196.0
Arsenic	1.83	19.9	0.081
Barium	397	8510	5.12
Boron	29.4	180	3.10
Cadmium	0.153	0.85	0.016
Calcium	46700.	425000	1510.
Chromium	11	192	0.111
Copper	14	63.2	0.581
Iron	19600	208000	2360
Lead	4.24	78	0.542
Magnesium	3440	24100	262
Manganese	484	123000	26.2
Mercury	0.268	1.86	0.022
Nickel	21.3	98.1	1.28
Potassium	699	5980	109
Selenium	0.267	1.87	0.06
Silicon	1640	111000	189
Silver	0.26	1.87	0.06
Sodium	529	5270	22.3
Strontium	93.4	981	11.9
Vanadium	29.9	178	1.25
Zinc	74.6	283	3.4
Chloride	1250	18100	0.723
Sulfate	396	8820	0.292

TABLE 2.3: NATURAL SOURCES OF ATMOSPHERIC EMISSIONS
(10⁶ gm/year)⁶

ELEMENT	CONTINENTAL DUST FLUX	VOLCANIC DUST FLUX	VOLCANIC GAS FLUX
Aluminum	356500	132750	8.4
Arsenic	25	3	0.1
Cadmium	2.5	0.4	0.001
Chromium	500	84	0.005
Cobalt	40	30	0.04
Copper	100	93	0.012
Iron	190000	87750	3.7
Lead	50	8.7	0.012
Manganese	4250	1800	2.1
Mercury	0.3	0.1	0.001
Nickel	200	83	0.0009
Selenium	3	1	0.13
Silver	0.5	0.1	0.0006
Tin	50	2.4	0.005
Titanium	23000	12000	--
Vanadium	500	150	0.05
Zinc	250	108	0.14

TABLE 2.4: METAL RELEASE RATES (kg/ha/yr)²

LAND USE	Zn	Pb	Cu
Business Distr.	2.90-2.99	6.66-6.84	-----
Shopping Center	3.15-3.24	2.72-2.81	-----
Multiple Family	0.31-0.39	0.68-0.84	-----
High-rise			
Residential	1.03-1.15	1.72-1.91	-----
Single Family	0.10-0.20	0.12-0.23	-----
Agriculture	0.005-0.30	0.002-0.08	0.002-0.09
Cropland	0.026-0.083	0.005-0.006	0.014-0.064
Pasture	0.019-0.172	0.004-0.015	0.021-0.038
Forest	0.01-0.03	0.01-0.03	0.02-0.03

TABLE 2.5: SOME METALS IN INDUSTRIAL WASTE STREAMS⁴

INDUSTRY	As	Cd	Cr	Cu	Pb	Hg	Se	Zn
Mining/Metallurgy	X	X	X	X	X	X	X	X
Paints/Dyes		X	X	X	X	X	X	
Pesticides	X				X	X		X
Electrical/ Electronic				X	X	X	X	
Cleaning/Duplicate	X		X	X	X		X	
Electroplating/ Finishing			X	X			X	
Chemicals			X	X		X		
Explosives	X			X	X	X		
Rubber/Plastics						X		
Batteries		X			X	X		
Pharmaceuticals	X					X		
Textiles			X	X				
Petroleum/Coal	X				X			
Pulp/Paper						X		
Leather			X					

**TABLE 2.6: CLASSIFICATION OF ELEMENTS ACCORDING TO THE
RATIO: RATE OF MINING/RATE OF NATURAL CYCLING²**

RATIO <10	RATIO >10
Arsenic	Cadmium
Cobalt	Gold
Iron	Lead
Molybdenum	Manganese
Nickel	Mercury
Uranium	Silver
	Tin
	Zinc

TABLE 2.7: METALS IN INDUSTRIAL WASTEWATERS (ppm)³

INDUSTRY	Cu	Cr	Ni	Zn	Cd
Meat Processing	150	150	70	460	11
Fat Rendering	220	210	70	460	6
Bakery	150	330	430	280	2
Misc. Foods	350	150	110	1100	6
Brewery	410	60	40	470	5
Soft Drinks/ Flavoring	2040	180	220	2990	3
Ice Cream	2700	50	110	780	31
Textile Dying	37	820	250	500	30
Fur Dressing	7040	20140	740	1730	115
Chemicals	160	280	100	800	27
Laundry	1700	1220	100	1750	134
Car Wash	180	140	190	920	18

**TABLE 2.8: EMISSIONS FROM FUEL COMBUSTION
AND INDUSTRIAL ACTIVITIES (10^6 gm/year)⁶**

ELEMENT	INDUSTRIAL PARTICLES	FOSSIL FUEL FLUX
Aluminum	40000	32000
Arsenic	620	160
Cadmium	40	15
Chromium	650	290
Cobalt	24	20
Copper	2200	430
Iron	75000	32000
Lead	16000	4300
Manganese	3000	160
Mercury	50	60
Nickel	600	380
Selenium	50	90
Silver	40	10
Tin	400	30
Titanium	3600	1600
Vanadium	1000	1100
Zinc	7000	1400

TABLE 2.9: METAL EMISSIONS (10^8 gm/year) FROM
COMBUSTION OF FOSSIL FUELS AND CEMENT PRODUCTION³

METAL	COAL	OIL	CEMENT PRODUCTION
Arsenic	46.0	0.1	29.3
Cadmium	1.3	0.0	0.7
Chromium	12.7	0.5	--
Cobalt	6.4	0.3	--
Copper	19.1	0.2	--
Lead	31.8	0.5	272.7
Mercury	3.6	14.6	0.9
Nickel	19.1	14.6	--
Selenium	3.8	0.3	6.4
Vanadium	31.8	74.6	--
Zinc	63.6	0.4	272.7

CHAPTER 3: PETROLEUM INDUSTRY SOURCES

The segments of the petroleum industry being reviewed in this report are exploration and production. The petroleum industry is a source for a number of heavy metal inputs into the environment. These metals include: arsenic, barium, cadmium, chromium, iron, lead, mercury, nickel, vanadium, and zinc. Metals are introduced primarily through the disposal of drilling muds and produced water. Other sources of metals are from waste oils, air pollutants from combustion engines, completion fluids, and drill cuttings. Heavy metals are also contained in paints used to protect equipment and in lube oil in the engines to run drilling and production equipment. The input of metals from the exploration and completion processes are a function of number of wells drilled and depth of the wells.

The amounts of heavy metals introduced into the environment and the problems associated with them are examined in the order of the natural progression of hydrocarbon production: drilling and production.

3.1 DRILLING OPERATIONS

Drilling operations include setting up the rig, making up the drill string, and the actual drilling of the well. Metals are contained in the drilling fluids and pipe dope used to drill the well. The drill cuttings produced from the formation are also covered with the drilling fluid containing heavy metals. These three elements are the primary sources of heavy metals during the drilling operations. The well location is a factor in determining the potential hazards associated with disposal of the metals.

3.1.1 DRILLING MUD: Drilling mud contains a number of metals, including arsenic, barium, cadmium, chromium, lead, and zinc.⁷ The concentrations and types of metal compounds vary widely among mud types. Barium is the most prevalent metal in drilling muds. It is found in barite or barium sulfate used to weight the fluids. Zinc is found in zinc bromide and zinc chloride used as dense salt solutions. Chromium is found in zinc chromate, a corrosion inhibitor, and in cross-linking agents that contain chromic chloride and chromium

potassium sulfate. Compounds of arsenic, lead, and cadmium are not specifically added to drilling fluids, but often occur as trace contaminants from the formation, or from other materials used in the drilling process such as pipe dope.

Pipe dope is used to makeup the drill string. Its purpose is to prevent damage to the threads of the drill pipe and it is almost always used in excess. The excess pipe dope is then washed into the drilling fluid as the well is drilled. Pipe dope generally has high concentrations of lead, zinc and copper. Table 3.1 lists approximate composition of several pipe dopes currently in use.

The locations of drilling sites can be divided into two classifications: on-shore and off-shore. A primary goal at on-shore sites is to prevent contamination of underground aquifers. On offshore platforms, the goal is to not harm the marine community.

3.1.1.1 ONSHORE: In onshore drilling activities,

the drilling fluid has historically been disposed of in on-site reserve pits. The rate of migration of heavy metals from these pits and their migration path determines the extent of their impact on the environment. If significant amounts of metals leach from the reserve pit, groundwater can become contaminated. The impacts on the environment can be estimated by determining the solubilities of the metals in the pit and how far the metal ions will migrate.⁷

3.1.1.2 OFF-SHORE: To prevent harm to marine communities, the discharge of oil-based muds is prohibited on the outer continental shelf, while the discharge of water-based muds is currently permitted.⁸ The presence of heavy metals in the muds is an important factor in their toxicity.

A 96-hour Acute toxicity test with mysid shrimp is used to determine the toxicity of the mud discharges. The results of the toxicity test are reported as LC₅₀ values, or the concentration of the mud in which 50 percent of the test organisms die within a 96 hour

period. The classification system developed for these tests is included in Table 3.2. The bioassay results from the Mid-Atlantic program, listed in Table 3.3, show that the suspended particulate phase is generally more toxic than the liquid phase, ie. the LC_{50} for the suspended particulate phase is lower.

One of the reasons that the particulate phase is more toxic could be from the toxic metals that have preferentially adsorbed to the particles. The duplicate numbers on Table 3.3 are results from two separate laboratory tests for each mud type. The difference in the values is an indicator of the accuracy of the testing procedures. As seen in Table 3.3, the majority of drilling fluids are non-toxic and have an LC_{50} of greater than 1,000,000 ppm. 1,000,000 ppm is pure drilling fluid. The test results apply for salt water discharges only because they were completed using the mysid shrimp. A similar protocol exists for testing fresh water discharge using the daphnia dubia, or water flea, and the fatheaded minnow.

The Generic Mud concept was developed so that all muds did not have to be tested for toxicity for

permitting of offshore drilling discharges. It defined eight basic mud types that encompassed most of the water based muds used on outer continental shelf. Tables 3.4 lists typical concentrations of metals present in each of the basic mud types defined in the Generic Mud Concept. The concentration of metals in the generic muds are all low, except for barium. Barium is the primary component of barite which is used to weight the mud. These tables do not, however, identify the bioavailability of these metals. Similar concentrations of metals are present in drilling muds used for on-shore applications.

3.1.2 DRILL CUTTINGS: Drill cuttings are the formation fragments removed from the wellbore during drilling. The cuttings contain naturally occurring metals and are coated with drilling fluids that contain metals. The concentrations of heavy metals contained in cuttings is dependent upon the type of drilling fluid and the additives used, and the naturally occurring metal level of the formation being drilled. Drill cuttings are disposed of differently for off-shore and

on-shore operations.

The drill cuttings from wells drilled off-shore are generally disposed of by dumping the cuttings overboard onto the sea floor. Disturbances to the benthic community remain high up to 500 meters from the discharge point for all mud types, while impacts from oil-based mud cuttings can be observed up to 12,000 meters from the discharge point.⁹ The greatest impacts are near the platform and are caused by physical smothering and sediment overload of existing biota with cuttings.

Oil from drilling mud and the formation is often trapped in the cuttings. Up to 93% of the discharged oil remains with the cuttings when discharged. This oil is not released to the upper water column due to the surface interactions between the wastes and the sediments. Therefore, the metals in the oil are not dissolved in the water column and will remain preferentially adsorbed to sediment particles. Metals in oil are discussed in section 3.2.2.

The disturbances to the benthic communities from the discharge of cuttings on the sea floor can be

directly related to the concentration of cuttings. High concentrations of oil-based cuttings smother bacteria and reduce pore water exchange which leads to a reduction in biotic activity.¹⁰ If the concentration of metals in the cuttings is too high, there can be a toxic reaction from the local bacteria.

The long term chronic effects from the discharge of cuttings into the sea are not clear. Studies have shown that bottom dwelling fish around the platform have some bioaccumulation of metals, while the pelagic fish do not.¹⁰ Oil-based liquids more readily bioaccumulate and/or absorb into fish tissues than the synthetic liquids which have been used as a drilling fluid base. The oil-based liquids are more toxic because of their greater bioaccumulations. However, the growth rate of the fish were affected by both types liquids. A more in-depth study of the lower toxicity synthetic liquids is needed, however.^{10,11}

One study reported the amounts of heavy metals released through the disposal of drill cuttings.¹² The concentrations of metals found in the drill cuttings after they were washed and were ready for disposal, are

shown in Table 3.5. By comparing these concentrations to those in Tables 2.1 and 2.2, it can be seen that the metals concentration of the cuttings was similar to the metal concentration of native soils and gravels. Therefore, if the cuttings are properly cleaned, they provide no higher risk from heavy metals than native soils.

3.2 PRODUCTION

The primary waste in the production process is produced water. However, crude oil and other materials also introduce metals into the environment.

3.2.1 PRODUCED WATER: The primary waste product in the production process is produced water.^{13,14} Most on-shore produced water is reinjected into the producing formation, while most off-shore produced water is discharged directly into the ocean from the platforms. The volumes and chemical composition of the produced water depends upon the location of the well and the characteristics of the producing formation.

The composition of produced water from two

platforms is given in Table 3.6. From this table it can be seen that the metal concentrations are generally higher than that of seawater. Through acute toxicity testing, it has been found that the metals provided little contribution to acute toxicity of the produced water. The toxicity of the produced water is primarily due to the high salt content. The metals were not present in produced water in bioavailable forms, but were adsorbed to particulates in the water. These insoluble forms of metals were not a significant factor in toxicity of the produced water. The materials of primary toxicological importance are soluble.¹⁴

Elevated concentrations of heavy metals in the sediments have been observed surrounding the platforms, but not in the water column around platforms. The metals were tightly sorbed onto the sediments and were not available to marine life.¹³ The concentrations of inorganics in the produced water increased as the gas reservoirs become depleted.¹⁴ Therefore, the discharged waters could become more toxic as the reservoirs deplete.

An alternative to reinjecting produced water into

the producing formation is to discharge the water into surface waters. A study has been conducted in Wyoming to investigate and document the beneficial use of produced water discharge and its effects when discharged into surface waters.¹⁵ In this study the receiving stream was classified by the state as having low aquatic value. In this case, whole-effluent toxicity testing prior to discharge was not required, although the discharge was required to meet NPDES requirements of total dissolved solids (TDS) of 5,000 mg/l; chloride, 2,000 mg/l; sulfates, 3,000 mg/l; oil and grease, 10 mg/l. This study supports the use of produced water discharge for beneficial use in agricultural areas where water is scarce.

3.2.2 CRUDE OIL: Crude oils contain variable concentrations of heavy metals, including aluminum, calcium, copper, iron, nickel, uranium and vanadium.¹⁶ The metals are complexed in the porphyrin compounds. Table 3.7 exhibits the variations in concentrations and physical characteristics of crude oil from three locations. Compared to the average ranges of metal

content listed in Table 2.1, the metal content of the crude oil are is similar to the metal content of freshwater, and lower than the metal content of seawater.

3.2.3 OTHER WASTES: Other wastes can be generated during production from improved oil recovery methods. Equipment used to generate steam for thermal recovery has waste waters that also must be disposed. Table 3.8 contains the typical composition of wastewater from steam generators. Waters from the steam generators are of poorer quality than produced water. These wastes may have to be disposed of by methods other than reinjection to the formation.¹⁷ The standards for reinjecting such waters is dependent on the permitting requirement of the area.

Electrical generators and other combustion engines can use refined crude oil for their operation. Refined crude oil also contains metals. The composition of two grades of fuel oils are shown in Table 3.9. By comparison to the crude oil composition in Table 3.7 it

can be seen that the metal composition of different oils can vary greatly and are also similar to the concentrations naturally occurring in freshwater and seawater.

3.3 TOTAL AMOUNTS OF HEAVY METALS GENERATED

While the concentrations of metals are important in determining the toxicity of a waste at a specific disposal site, the total quantities of heavy metals released into the environment is also important. In the United States, 21 billion barrels of produced water are produced annually, and 361 million barrels of drilling waste are generated. These figures are based on 1990 data.¹⁸ Table 3.10 lists the heavy metals present and the total amounts generated in the United States oil exploration and production processes.

The petroleum industry does not introduce a significant amount of metals to the environment when compared to the natural and man-made sources discussed in Chapter 2. For many of the metals, the amounts generated through natural processes are several magnitudes higher.

TABLE 3.1: COMPOSITION OF PIPE DOPE^{1 2}

CONSTITUENT WT%	BML26DS	LEAD 60%	ZN 50%	COPPER BASED
Grease	40%	25%	45%	60%
Microspheres	57%	--	--	--
Graphite	3%	3%	--	--
Copper	--	--	--	20%
Lead	--	65%	--	--
Zinc	--	--	52%	--
Misc.*	--	7%	3%	20%

*includes non-functional fillers and stiffeners

TABLE 3.2: CLASSIFICATION OF TOXICITY GRADES^a

	LC ₅₀ VALUE (ppm)
Practically Nontoxic	>10,000
Slightly Toxic	1,000 to 10,000
Moderately Toxic	100 to 1,000
Toxic	1 to 100
Very Toxic	<1

**TABLE 3.3: 96-HOUR LC₅₀ for MYSID SHRIMP RESULTS
FROM MID-ATLANTIC BIOASSAY PROGRAM^a (ppm)**

GENERIC MUD TYPE	LIQUID PHASE	SUSPENDED PARTICLE PHASE
1. Potassium/Polymer	66,000	25,000
	58,000	70,900
2. Lignosulfate Seawater	283,500	53,200
	880,000	870,000
3. Lime	393,000	66,000
	>1,000,000	860,000
4. Nondispersed	>1,000,000	>1,000,000
	>1,000,000	>1,000,000
5. Seawater Spud	>1,000,000	>1,000,000
	>1,000,000	>1,000,000
6. Seawater/Freshwater	>1,000,000	>1,000,000
Gel	>1,000,000	>1,000,000
7. Lightly Treated	>1,000,000	>1,000,000
Lignosulfate	>1,000,000	>1,000,000
Fresh/ Sea		
8. Lignosulfate	>1,000,000	560,000
Freshwater	>1,000,000	>1,000,000

Note: the two values for each mud type are the results from two separate laboratory tests.

TABLE 3.4: METALS CONTENT OF GENERIC MUDS (ppm)^a

MUD TYPE	As	Ba	Cd	Cr	Cu	Pb	Hg	Ni	V	Zn
1. Potassium/Polymer	1	24,000	<1	14	2	2	<1	6	9	20
2. Lignosulfate Seawater	2	141,000	<1	227	11	<1	<1	8	18	181
3. Lime	3	76,200	<1	192	8	4	<1	3	27	58
4. Nondispersed	2	13,300	<1	10	7	2	<1	4	22	16
5. Seawater Spud	3	28,000	<1	16	5	4	<1	6	35	21
6. Seawater/ Freshwater Gel	2	25,600	<1	2	2	<1	<1	1	6	12
7. Lightly Treated Lignosulfate Fresh/ Sea	<1	11,500	<1	265	26	24	<1	6	30	82
8. Lignosulfate Freshwater	3	14,000	<1	48	4	9	<1	8	18	15

**TABLE 3.5: CONCENTRATION OF ELEMENTS FOUND IN
PROCESSED DRILL CUTTINGS (mg/kg dry)¹⁹**

ELEMENT	MINIMUM	MAXIMUM	MEAN
Aluminum	448	7230	3839
Arsenic	3.02	11.6	7.31
Barium	40.1	1510	775.1
Boron	20.7	37.9	29.3
Cadmium	0.21	0.39	0.30
Calcium	150	5800	2975
Chromium	0.836	16	8.418
Copper	3.5	32.8	18.2
Iron	972	15900	8436
Lead	2.11	58.2	30.16
Magnesium	132	4030	2081
Manganese	8.53	289	148.77
Mercury	0.259	0.33	0.295
Nickel	3.21	27.2	15.21
Potassium	126.0	1200.0	663.0
Selenium	<0.308	<0.308	----
Silicon	188.0	2320.0	1254.0
Silver	0.416	0.53	0.473
Sodium	277	1820	1048.5
Strontium	51.9	66.5	59.2
Vanadium	1.09	45	23.05
Zinc	6.41	152	79.21

TABLE 3.6: ELEMENTAL COMPOSITION OF DISCHARGE FROM TWO PLATFORMS IN THE NORTH SEA (mg/l)²⁰

SAMPLE	PLATFORM A	PLATFORM B	TYPICAL SEAWATER
Aluminum	<1.0	1.2	0.01
Antimony	<0.005	0.01	0.0003
Barium	0.3	<1.0	0.03
Beryllium	<0.06	<0.06	0.0000006
Boron	0.7	34.0	4.6
Calcium	8.4	460.0	400.0
Cadmium	<0.005	<0.005	0.0001
Cobalt	<0.3	<0.3	0.0003
Chromium	<0.01	0.06	0.00005
Copper	<0.08	<0.08	0.003
Iron	42.0	0.55	0.01
Lead	<0.05	<0.05	0.00003
Magnesium	9.2	350.0	1350.0
Manganese	2.5	0.49	0.002
Molybdenum	0.01	<0.01	0.01
Nickel	0.21	0.03	0.005
Silicon	0.2	26.0	3.0
Silver	<0.1	<0.1	0.0003
Sodium	80.0	8300.0	10500.0
Strontium	<5.	41	8.1
Tellurium	<0.02	<0.02	--
Tin	0.03	<0.005	0.003
Titanium	<0.1	<0.1	0.001
Uranium	<0.005	<0.005	0.003
Vanadium	<0.04	<0.05	0.002
Zinc	<0.15	<0.15	0.01

**TABLE 3.7: PHYSICAL CHARACTERISTICS AND CHEMICAL
PROPERTIES OF SEVERAL CRUDE OILS
(EXCLUDING HYDROCARBONS)¹⁶**

CHARACTERISTIC OR COMPONENT	PRUDHOE BAY	SOUTH LOUISIANA	KUWAIT
API Gravity (20 C)	27.8	34.5	31.4
Sulfur (wt%)	0.94	0.25	2.44
Nitrogen (wt%)	0.23	0.69	0.14
Nickel (ppm)	10.0	2.2	7.7
Vanadium (ppm)	20.0	1.9	28.0

TABLE 3.8: TYPICAL COMPOSITION OF WASTEWATERS FROM STEAM GENERATORS¹⁷

COMPONENT	CONCENTRATION (PPM)
Aluminum	0.4
Bicarbonate	31,183.0
Boron	20.8
Calcium	11.2
Carbonate	0
Chloride	2,237.3
Copper	0.5
Flouride	5.2
Iron	32.0
Magnesium	0.43
Manganese	0.63
Nitrate	0.5
Phosphate	0.6
Potassium	101.0
Sodium	53000.0
Sulfate	79,013
Sulfur Dioxide	420.0
Total Dissolved Solids	148,438.0
Zinc	5.3

**TABLE 3.9: PHYSICAL AND CHEMICAL PROPERTIES
OF TWO REFINED PRODUCTS¹⁶**

CHARACTERISTIC OR COMPONENT	NO.2 FUEL OIL	BUNKER C FUEL OIL
API Gravity (20 C)	31.6	7.3
Sulfur (wt %)	0.32	1.46
Nitrogen (wt %)	0.024	0.94
Nickel (ppm)	0.5	89.0
Vanadium (ppm)	1.5	73.0

**TABLE 3.10: AMOUNT OF HEAVY METALS DISPOSED IN
THE UNITED STATES^{7,8,13,14,18} (10³ gm/year)**

ELEMENT	PRODUCED WATER	DRILLING WASTES	TOTAL
Silver	0.41	NR	0.41
Aluminum	41.33	NR	41.33
Barium	12.40	31865.4	31877.7
Calcium	347.22	NR	347.22
Cadmium	0.21	<0.1	0.3
Cobalt	12.40	NR	12.4
Chromium	0.41	1.76	2.2
Copper	0.02	6.72	6.7
Iron	1735.86	NR	1735.86
Lead	2.07	4.86	6.9
Magnesium	380.24	NR	380.24
Manganese	103.32	NR	103.32
Molybdenum	0.41	NR	0.41
Nickel	8.70	4.34	13.0
Sodium	3305.40	NR	3305.4
Strontium	206.7	NR	206.7
Tin	12.40	NR	12.4
Uranium	0.21	NR	0.21
Vanadium	1.65	17.04	18.9
Zinc	6.2	41.83	48.0

NR is for values that were not reported.

CHAPTER 4. TRANSPORT PHENOMENA

The primary threat from heavy metals is from their migration from waste disposal or emission sites. This migration exposes a larger environment, primarily humans, to the metals. The main methods of migration include transport of dissolved metals in groundwater and surface water, and transport of particles and vapors through the atmosphere.

Once a heavy metal has been introduced into the environment, it can interact with the materials encountered. The most common materials encountered are surface water, pore water, and soil. The ease with which a metal can be transported can be related to its geochemical mobility. Geochemical mobility is defined as the tendency of an element to move in natural water and remain in a stable, dissolved state relative to the mean content of the crust and hydrosphere. Table 2.1 classifies heavy metals according to their geochemical mobility. For example, the elements arsenic, antimony, molybdenum and silver have a high geochemical mobility, and therefore tend to remain as dissolved solids rather than interacting with the solids.

During transport, the concentrations of metals can be enriched through various chemical reactions with water and solids. This occurrence is often reported in terms of enrichment factors, EF. Enrichment factors are the concentration of a metal in a sample relative to the concentration in some reference sediments. The concentrations and EF's can be contoured and the extent of contamination mapped.²¹

The reason for determining the mobility and chemical reactions of heavy metal wastes is to predict adverse effects in the environment. Soil cleanup standards that require cleanup to background concentration often assume that the soil is already at its maximum carrying capacity for immobilizing the metal. This is often incorrect because the background concentrations are based solely on the amount of elements present during the soils construction, not how much additional metal it can retain.

Metals concentrations in soil are normally determined using the Toxicity Leach Characteristic Procedures, TLCP, or the EP-TOX tests as outlined by the Environmental Protection Agency. These tests

determine only a fraction of the soluble metal concentrations present in the soil. However, the test results have no basis for determining the extent of metal migration and possible chemical reactions in the soil, and are not designed to provide this information. Other protocols exist to determine the mobility potential of heavy metals.

4.1 TRANSPORT THROUGH SURFACE WATERS

Heavy metals being transported by water are present either as soluble ions or adsorbed onto suspended particles. Metals adsorbed onto suspended particles is the primary method of transport through surface waters.² However, there are three major factors which affect the distribution of trace metals between the solution and particles: (1) the chemical form of the dissolved metals, (2) the type of interactive processes between metals and mediums, and (3) the composition and concentration of the particles, primarily with respect to surface reactions.⁴

Both suspended particles in surface waters and associated sediments can effect the concentrations of

heavy metals present. Sediments can act as storage for metals and are an additional source of metals for the adjacent water and biota. This source of contamination was recently identified and is also considered a non-point source.²

Because heavy metals are continually released by sediments, they will, in time, clean themselves if the input of contaminants is stopped. The residence times of contaminants in the water and sediments of rivers and lakes are very different and are functions of the discharge rate, stream velocity, and morphology of the waterways. Rivers have much shorter residence times than lakes; especially deep lakes.² Bioturbation also speeds the release of contaminants from the sediments.

4.2 TRANSPORT THROUGH GROUNDWATER

Factors that govern the solubility and mobility of metals in soils and fluids includes soil permeability, depth to the water table, rates of precipitation and evaporation, type and volume of wastes, and the geochemical characteristics of the soil and fluid. The behavior of toxic metals in the aqueous phase of wastes

and soils depends on the form of chemical compound more than concentration. Parameters which govern the behavior of metals include pH, type and concentration of complexing agents, and oxidation state of the components. The pH and redox potential of the system are both important in the speciation of an element. Oxidized forms of a metal are usually more soluble than reduced forms, although there are exceptions.

Soil and waste systems are complex electrolytic solutions with a number of inorganic and organic ligands. The soluble fraction of the toxic metals in the system will exist in both the free aqueous forms and as complexes with the ligands. Ligands are organic or inorganic molecules or ions which form metals complexes under certain circumstances.⁶ The concentration of these ligands will have a direct effect on the total quantity of metals in solution and can enhance the solubilities of the metals by several orders of magnitudes over the calculated solubilities of their soluble salts.⁷

Soluble hydrolysis products are important in solutions containing trace metals. Metals in aqueous

solutions generally hydrolyze to form mononuclear and polynuclear hydroxy complexes. The general chemical equation is $xM^{n+} + yH_2O = M_x(OH)_y^{n-y} + yH^+$. Hydrolysis equilibrium is established quickly for simple species, but polynuclear complexes often form slowly. For many metals, the polynuclear species are formed only under conditions of oversaturation with respect to metal hydroxide or metal oxide and are therefore not stable thermodynamically.⁷

Soluble metals ions are potentially more hazardous because they are more bioavailable. Table 4.1 compares the relative solubility of elements being transported in rivers. In this table, the transport index is defined as the fraction of the metal which is present in a dissolved state as compared to the total amount of metal present. The total amount of the metal present is the combination of metals in solution, metal adsorbed to particles, and metals present in the particles. The more toxic metals include cadmium, lead, hexavalent chromium, and cobalt.^{1,2,4} From this table it can be seen that the toxic metals preferentially adsorb to particles in the water, making them less bioavailable.

The solubility, mobility, and bioavailability of metals bound to sediments can be increased in four ways:

- (1) lower the pH,
- (2) increase salt concentrations to increase the competition for sorption sites,
- (3) increase the occurrence of complexing agents,
- (4) change the redox conditions.

The total concentration of an inorganic chemical in soil is:

$$C_{total} = C_{fix} + C_{ads} + C_{water}$$

where, C_{fix} = concentration fixed in the structure of the soil mineral grains.

C_{ads} = concentration adsorbed onto the mineral surface

C_{water} = soluble fraction in the pore fluid in equilibrium with C_{ads}

The fixed portion of metals in soil is composed of the concentration adsorbed to clay, the concentration adsorbed onto oxides, the concentration adsorbed onto organic matter, the concentration of oxide occluded, the concentration of biologically occluded, and the concentration in the mineral lattice.

4.3 SOIL AND FLUID INTERACTIONS

When soils and fluids are contacted with heavy metals, whether as bottom sediments or in groundwater, metal-particle interactions occur. These interactions include adsorption, desorption, precipitation, ion-exchange and complexation. The environmental variables which can affect the reactions include: pH, temperature, and pressure. Ion exchange and adsorption are affected by pH because the hydrogen ions compete for the available sites. Because many elements can exist in several valence states, the redox potential, or Eh, is used to measure the extent to which species in solution are electron-rich or deficient. This determines which species are available for sorption, precipitation, or complexation.⁷ These basic processes are discussed in the following subsections.

4.3.1 ADSORPTION: Adsorption is the process of metal ions attaching to vacant charge locations on soils. The amount of metals adsorbed is a function of the soil type and can be analytically determined. The

pH of the pore water is the controlling factor in sorption-desorption processes. The adsorption equilibrium coefficients are a function of sediment type. The following equilibrium reactions describe the concentration of surface species which effect the adsorption:



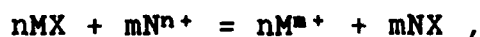
Metal concentrations in soil depend on the grain size distribution, with higher trace metal levels being associated with smaller grains. The smaller grains have a larger surface area per volume of rock, and consequently, they have a greater number of surface exchange sites. Coarser silicates contain almost no trace metals.²¹

Adsorption-desorption processes can be impacted by the degradation of organic matter, the transformation of iron and manganese oxyhydrates to sulfides and the reverse, and the biotransformation of contaminants ingested by organisms.^{2, 6, 7, 22}

4.3.2 CATIONIC EXCHANGE: Cation exchange is a surface phenomena and depends on soil composition. The

amount of cation exchange is characterized by the Cationic Exchange Capacity or CEC of clays. The amounts and types of clays present is very important because of their high cationic exchange capacities.⁷ Table 4.2 lists the CEC's of some common clays.

The equilibrium between the soil solution and the exchangeable cations of the clays can be described as:



where M and N are metals cations with charges of m^+ and n^+ , and MX and NX are metals sorbed onto the solid surface.

4.3.3 DIFFUSION OF METALS IN SOIL MINERALS: The diffusion process can lead to irreversible adsorption and can cause heavy metals to become immobilized and unavailable. In this process, the cations that are bound to the surface of a mineral grain are diffused into its interior structure. The chemical makeup of the mineral is then changed.^{5,6}

4.3.4 COMPLEXATION: Metal complexes are formed when water ligands are replaced by other molecules. The

pH of the water determines the availability of ligands for complexation with metal ions. Metal binding can occur with the sediment by complexation of metals ions with the charged functional groups or ion exchange of metal ions for hydrogen ions (based on the multi-site binding model used).^{6,7,22}

4.3.5 PRECIPITATION: Precipitation occurs when the pore water or carrying fluid becomes supersaturated with respect to a compound or element and a solid is dropped out of solution to return the system to equilibrium. Precipitation reactions are well documented as a mechanism for metal fixation.^{6,10}

4.4 ATMOSPHERIC TRANSPORT

Heavy metals can also be transported through the air. Atmospheric transport is dependent on particle size and atmospheric conditions. It is readily apparent that for the high specific gravity metals to be transported by air, the particle size must be very small. The dust particle concentration has been found to decrease with distance from the source.²²

One study simulated the total atmospheric inputs of lead and cadmium in the North sea using a 3-D transport model. The amount of metals introduced into the atmosphere as calculated by the model were much lower than the amount predicted by extrapolations from measured precipitation amounts and rainwater concentrations along the coasts. Accurate measurement of metals emissions and advanced mathematical modeling is required to predict the transport of metal in the atmosphere.²³

4.5 STUDIES OF METAL TRANSPORT

In one four year study of heavy metal transport through the environment, the leaching and upward transport of several metals in cores was studied.²³ Two different types of cores were used, a leaching core and a groundwater or capillary rise core. The study reported that the amounts of leachate decreased as a percentage of total rainfall from 46% in year one to 30% in year four. The larger amounts of early leachate were probably from the initial disturbances of the soil upon construction of the cores. The compaction of soils

over time must be considered when constructing a solid waste facility or land farming treatment facility. It was also found that the elemental mobility in the leaching cores for year 4 decreased in the order $Cr > Mo > U$. The study also indicated that there can be a synergistic effect when multiple metals are present, particularly chromium and molybdenum.

Another study reported that adsorption of cadmium onto natural solids is important in minimizing toxic potential from cadmium emissions.²² This study also reported that sediments are negatively charged over a wide range of pH and surface charge density increases approximately linearly with pH.^{22, 23, 25} The increase in surface charge density increasing the number of sites for metal ions to become adsorbed and less bioavailable. Cadmium was found to be adsorbed onto only a fraction of the hydrolyzed sites and that the maximum adsorption of cadmium is a function of sediment type.

The potential pollution problems caused by the heavy metals present in drilling fluids has been analyzed using a geochemical flow simulator based on

local thermodynamic equilibrium.⁷ The model assumed one dimensional flow, incombustible fluids and solids, isothermal homogeneous medium, local thermodynamic equilibrium, no activity corrections, and no migration of solids. The conclusions of the study were:

1) the maximum soluble amount of arsenic in a drilling waste is primarily dependent on the concentration of barium. The concentration of barium required to keep arsenic concentration low increases as the pH and Eh decrease.

2) the concentration of soluble barium is very low when the sulfate content exceeds 1.5 mg/L. The soluble barium will readily form BaSO_4 and $\text{Ba}_3(\text{AsO}_4)_2$.

3) The solubility of cadmium is controlled by the presence of CO_3^{2-} . Chloride concentration also impacts the solubility of cadmium because of the formation of cadmium chloride complexes.

4) The solubility of chromium is controlled by the presence of OH^- .

5) The solubility of the metals in reserve pits can be kept low by keeping the pH of the system greater than or equal to 6.5.^{7,10}

**TABLE 4.1: DISSOLVED TRANSPORT INDEX IN RIVERS.
PERCENTAGE OF THE CONCENTRATION OF DISSOLVED ELEMENT
RELATIVE TO THE TOTAL AMOUNT PRESENT.²**

% DISSOLVED/TOTAL	ELEMENTS
90-50	Br, Ca, Cl, I, Na, S, Sr
50-10	As, B, Ba, Cu, F, K, Li, Mo, Mg, N, Sb, Zn
10- 1	Co, Cr, Cs, Mn, Ni, P, Pb, Rb, Si, Th, U, V
1-0.1	Al, Ce, Er, Eu, Fe, Ga, Gd, Ho, La, Nd, Pr Sm, Ti, Yb

**TABLE 4.2: CATIONIC EXCHANGE CAPACITY
OF COMMON CLAYS^{6,7}**

MINERAL	EXCHANGE CAPACITY (meq/100G at pH 7)
Kaolinite	3 - 15
Montmorillinite	70 - 100
Illite	10 - 40
Vermiculite	100 - 150

CHAPTER 5. METAL CHARACTERISTICS AND TOXICITY:

Heavy metals are a concern in the environment because living organisms can exhibit adverse effects when exposed to a high enough concentration of them. While some metals are toxic to organisms, a number of metals are required for normal growth. An element is considered essential if it is consistently found in healthy living tissues within a zoological family, deficiency syndromes are detected upon depletion or removal of the metals, and the deficiency syndromes disappear when the elements are returned to the tissue.

The degree to which metals can affect organisms is controlled by their toxicity and availability. Toxicity is a measure of the effects on living organisms. Availability is a function of the occurrence and solubility of the metal. It is a measure of how much metal is present and how readily it can be dissolved in water. Metals which are insoluble cannot readily interact with living organisms or tissues and, therefore, are not bio-available. Table 5.1 lists some metals and classifies them according to availability and toxicity. The middle column lists the metals of

greatest environmental concern.

Living organisms that are exposed to increased concentrations of heavy metals often exhibit changes in their growth patterns and life span. The effects can be either chronic or acute. Some of the common effects are reduced growth, increase in mutagenic and carcinogenic occurrences, and a decrease in normal reproduction rates. The magnitude of the changes is related to the type of exposure, concentrations and speciation of the metals, and characteristics of the organism.

Bioaccumulation is the accumulation of metals in the tissues or organs of living organisms, and can be related to the exposure to heavy metals. An example of bioaccumulation is seen in vegetation grown in gardens contaminated with old mine tailings in Aspen, Colorado.²⁵ The amounts of lead and cadmium present in tailings were enough to be hazardous, if ingested. Vegetables grown in local gardens had concentrations that could pose health hazards, especially to children. The highest concentrations of these metals were in the leafy tissue, lower amounts in roots and tubulars, and the lowest levels were in the fruits. Broccoli and

cabbage, however, contained very low concentrations of lead.

To evaluate the environmental and human risk from a contaminant, a Quantitative Risk Assessment (QRA) can be completed. QRA evaluates potential human exposures to contaminants by evaluating incremental health risks. Risk is equated to hazard times exposure. The QRA process has four steps: hazard identification, dose-response assessment, exposure assessment, and risk characterization. All the possibilities of metal exposure must be calculated and combined with the available toxicity data to develop an accurate risk assessment. A detailed discussion of QRA can be found in reference 27.

The specific effects of a metal in different organisms can vary widely, but general effects are to alter growth, activity, and reproductive processes on all levels of tissue organization. The effects of exposure of humans to heavy metals can be divided into two categories; acute and chronic. Acute effects, or effects from a single exposure of high concentration, may include headaches, nausea, diarrhea, and vomiting.

In many cases, the metal is purged before further biologic damage or death occurs. Chronic effects, or effects from long term, low level exposures, include anorexia, nausea, vomiting, toxic pulmonary diseases, and respiratory and other organ specific cancers. Each metal has many particular conditions which can be related to distinct exposure levels and exposure paths.

Some metals have been found to be carcinogenic. These metals are beryllium, cadmium, chromium, cobalt, nickel, and lead. There is also evidence that arsenic is carcinogenic to humans, principally towards the lung and skin, but there have been no supporting tests on animals. Metals which are weakly to marginally carcinogenic at high dose levels are copper, manganese, molybdenum, silver, titanium, and zinc.¹

The effects of exposure to metals can also depend on the method by which the organism is exposed. The most common forms of exposure are inhalation, ingestion, and physical contact through skin tissue. The concentrations and chemical species of the metals are also a factor in determining the effects. Each metal is slightly different in its occurrences and

toxicity.

The toxicity of each metal is related to the biological reactions which occur in each organism. These biological reactions include making complexes and chelates. A complex is a chemical compound composed of group of metal ions and other chemical species that have formed a single structure. A chelate is a chemical compound in which the metal atom is attached to the neighboring atoms to form a ring structure. Metals and arsenic react with -SH groups and can form coordination complexes and chelates with various compounds and structures in the cell.¹

The -SH and coordination complexes and chelates formed in living organisms are called biocomplexes. The relative stabilities of complexes of some coordinating metals decrease in the order of: $\text{Hg} > \text{Be} > \text{Cu} > \text{Ni} > \text{Co} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn}$. The relatively high stability of mercury makes it highly toxic.¹

Metals also interact with ligands. A ligand is an inorganic or organic molecule or ion which forms complexes with metals ions under certain circumstances. Examples of ligands which are important include amino,

carboxyl, phosphoryl, imidazole groupings, Cl^- , $\text{SO}_4^{=}$, OH^- , and HCO_3^- . Organic ligands also exist which have donor atoms that will form complexes. An important endogenous heavy metal receptor is metallothionein, a low molecular weight protein, which is rich in $-\text{SH}$ groups. The exact cellular function is not known but has been suggested to be a "heavy metal scavenger".^{1,6}

Most sources of heavy metals add more than one type metal to the environment. The toxic effects of these combined inputs can vary greatly, depending on the metal species present. The terms synergistic and antagonistic are used to describe the toxicity resulting from reactions between metal species. A synergistic reaction will have an additive effect on the toxicity. An antagonistic effect will reduce the overall toxicity of the mixture.

The synergistic and antagonistic effects of metals have been examined and it has been found that antagonistic effects are the result of competition for $-\text{SH}$ groups and/or coordination ligands in the tissue. It was also determined that both effects are dependent on the concentrations of each metal present and will

change as the concentrations are changed.¹ The specific interactions vary extensively and also depend on whether the metal is essential for sustaining life.^{1,6}

5.1 SPECIFIC METAL CHARACTERISTICS

The following subsections will describe some of the specific characteristics of the heavy metals and their related toxicities.

5.1.1 ARSENIC: The speciation of arsenic is very important because the arsenic compounds have very different properties. The trivalent forms of arsenic are the most toxic. Arsenic compounds tend to form insoluble complexes with soils and sediments, however some leaching may occur. In petroleum reserve pits, arsenic and barium often form $\text{Ba}_3(\text{AsO}_4)_2$. The chronic effects of arsenic include mutagenicity, carcinogenicity and teratogenicity. Arsenic compounds are frequently used in pesticides, fungicides, and herbicides. Low solubility, organic arsenic compounds found in seafood are generally excreted in urine. The

hazards from inorganic compounds humans are exposed to from industrial operations are small to negligible. Water soluble inorganic compounds are readily absorbed through the stomach lining, lungs, and more slowly through the skin. Arsenic has been found to reduce the toxicity of selenium in the body. The fatal dose for ingesting arsenic trioxide is 70-180 mg.^{6,7}

5.1.2 BARIUM: Barium is most commonly found in the petroleum industry as barite (BaSO_4), which is very insoluble, except in acidic conditions. This low solubility makes its bioavailability very low. Specific exposure limits for humans were not available, however, the LD_{50} for oral exposure of rats is 921 mg/kg.^{6,7}

5.1.3 CADMIUM: Cadmium is highly toxic. The most important source of cadmium is through food. To limit the cadmium concentrations in food, many countries have put restrictions on agricultural soil concentrations for both the naturally occurring cadmium and any soil additives. Chronic inhalation effects include emphysema, and renal and kidney dysfunction. The World

Health Organization has recommended a biologic threshold value of 10 ug Cd/l of whole blood.^{6,7}

5.1.4 CALCIUM: Calcium is important in the function of the human body. It is present in the circulatory system, and a component in the formation of bones and teeth. Calcium is the most abundant metal in the human body.⁶

5.1.5 COBALT: Cobalt(III) complex makes up vitamin B₁₂, which is required by the body to form hemoglobin. Cobalt(II) is an enzyme activator. Inorganic cobalt salts, however, exhibit moderate toxicity to higher animals and man. Exposures to cobalt dusts, aerosols, and low solubility compounds have all been found to be carcinogenic. Allergic responses to exposure have also been identified that make Maximum Exposure Limits almost impossible to set. Tolerances of 0.01 to 0.1 mg/l for fish have been established.⁶

5.1.6 COPPER: Copper(I) is required in the formation of hemoglobin. Recommended daily intakes is

or 2.0 to 5.0 mg for adults, an 0.5 to 0.7 mg for infants.⁶

5.1.7 CHROMIUM: Chromium is essential for living organisms in the form of biologically active chromium, BAC, for the metabolism of glucose. The only important compounds are the trivalent and hexavalent compounds. Hexavalent chromium is 100 to 1000 times more toxic and is known to reduce plant growth, cause skin inflammations and eczemas, and lung cancer. Adsorption through the skin can cause bleeding of the stomach and intestine, serious liver and kidney damage, and cramps. An oral dose of 0.5 -1.0 gm of potassium dichromate is fatal for man. The toxicity data on trivalent chrome is less known. A dose of 35 - 350 gm of chromium chloride had no toxic effects on man.⁶

5.1.8 IRON: Iron is the most abundant metal in nature. Hemoglobin in blood is an iron complex. Humans are very susceptible to iron deficiency due to changes in diet from animal proteins to vegetable proteins. Iron overload is usually caused by malfunctions in the

bodies ability to adsorb and process iron. Amounts in excess of 200 mg/l have been found to be toxic to plants and humans.⁶

5.1.9 LEAD: Lead has been found to be very toxic and can affect energy metabolism and neurochemical and neurological functions. Infants and children are especially susceptible to lead. Microorganisms, such as soil bacteria, have been found to be more sensitive than plants to lead contents in soil. The changes in bacteria population can radically change the rates of decomposition at a specific site. Plants such as *Festuca rubra* and *Agrostis tenuis* have been found to thrive in lead-contaminated soils and have been used to stabilize toxic mine wastes with lead concentrations of 80,000 ug/g.^{6,7}

5.1.10 MAGNESIUM: Magnesium compounds are essentially nontoxic. Overdoses are usually eliminated by vomiting and diarrhea. Magnesium is also important in the function of the human body. It is required for nerve impulse transmissions, muscle contractions, and

metabolism, and various deficiency syndromes have been identified. The LD₅₀ of magnesium for dogs is 250 mg/kg. Magnesium fumes may be irritating.⁶

5.1.11 MANGANESE: Manganese is an essential element which is very rarely toxic. The maximum level of manganese has been recommended to be 1-1.5 mg/l, but undesirable taste and odor are prevalent at 0.5 mg/l, the EPA drinking water standard. The EPA drinking water standards are discussed below. Manganese is readily exchanged with magnesium in biologic systems. It is required to activate enzymes and is involved in the utilization of glucose.⁶

5.1.12 MERCURY: The low boiling point and high vapor point of mercury make it very mobile. There are three separate categories in which mercury has different properties: metallic mercury, inorganic ions of mercury, and organic mercury compounds. Metallic mercury has a high vapor pressure and solubility with water and certain lipid solutions and is, therefore, of

toxilogical importance. The toxicity varies greatly, depending on the type of mercury compound and the exposure. Acute toxic doses for humans ranges from 5 - 29 mg/kg of body weight, depending on the mercury compound. Neurological disorders are very common from mercury poisoning. Maximum allowable exposure ranges from: 0.05 mg/m³ of air for mercury vapor, to 0.1 mg/m³ of air for inorganic mercury salts, and 0.01 mg/100 mL of blood for methylmercury.⁶

5.1.13 MOLYBDENUM: Molybdenum does not occur natively as a pure metal, but instead in minerals like molybdenite, powelite, and wulfenite. Molybdenum is involved in the electron transfer processes in xanthine and purine oxidations in milk. Nitrogen fixation is also coupled to a molybdenum process. The levels of molybdenum toxicity are related to the quantities of copper and sulfates present in the organisms. Maximum exposures must be determined based on the relationship between copper, molybdenum and sulfates.⁶

5.1.14 NICKEL: Nickel is present in three types of

compounds: inorganic water-soluble, inorganic water-insoluble, and organic lipid-soluble. Nickel compounds are relatively insoluble at $\text{pH} > 6.5$, but are increasingly soluble with increasing acidity.⁶ Toxicity data for nickel was not available.

5.1.15 VANADIUM: Vanadium has been found to be essential for the rat and chickens, and is therefore, presumed to be essential to man. No deficiency syndromes have been noted in humans. Some organisms have been found to accumulate vanadium, but no purpose for this has been determined. Vanadium can be toxic if inhaled in large concentrations, but is not very toxic if ingested because it is not readily absorbed through the intestine.⁶

5.1.16 ZINC: Zinc appears to be present in all mammals, and functions as an essential constituent of many enzymes. To prevent deficiencies in humans, recommended dietary allowances of 10 mg/day for children and 15 mg/day for adults. A maximum tolerable allowance of 1.0 mg/kg of body weight has also been

established.⁶

5.2 REGULATORY LIMITS FOR METALS

The EPA has established drinking water standards for many constituents. The metal standards are listed in Table 5.2. These values are often used to determine the levels of metals that are permitted in the disposal of wastes. The drinking water standards for metals generally a factor of 10 lower than the average soil and water concentrations listed in Table 2.1. The concentrations listed in Table 5.2 do not consider metal species or interactions that occur with species that may alter its toxicity. The implicit assumption is that the most toxic species is present, which makes the standards conservative.^{6,7}

**TABLE 5.1: CLASSIFICATION OF METALS ACCORDING
TO TOXICITY AND AVAILABILITY²**

NONTOXIC VERY AVAILABLE	VERY TOXIC AND RELATIVELY AVAILABLE	TOXIC BUT VERY INSOLUBLE OR VERY RARE
Aluminum Calcium Chromium Iron Magnesium Potassium Sodium	Arsenic Barium Beryllium Cadmium Cobalt Copper Gold Lead Mercury Silver Tin Zinc	Barium Titanium

TABLE 5.2: U.S. DRINKING WATER STANDARDS (mg/l)⁶

ELEMENT	CONCENTRATION
Arsenic	0.5
Barium	1.0
Cadmium	0.01
Chloride	250.0
Chromium	0.05
Copper	1.0
Iron	0.3
Lead	0.05
Manganese	0.05
Mercury	0.002
Nickel	10
Selenium	0.01
Silver	0.05
Zinc	5.0

CHAPTER 6. MANAGEMENT OF HEAVY METALS

Point sources of heavy metals can be effectively controlled through monitoring, regulations, and technology.² Non-point sources of heavy metals must be controlled through monitoring and technology, because they do not have a specific source to regulate. The primary sources of metals discharged from the petroleum industry are point sources: disposal of drilling muds, drill cuttings, and produced water. A lesser amount of metals are released from oil spills on land and water.

Solutions to heavy metal pollution can be divided into four categories: hazardous waste minimization, recycling, replacement, and safe disposal. The goal of these categories is to reduce the amount used, find ways to recycle materials, substitute toxic materials with new less toxic materials, and find better ways to dispose of metals without harming the environment.

6.1 HAZARDOUS WASTE MINIMIZATION

Hazardous waste minimization is an important step in dealing with the growing problem of disposal and handling of hazardous wastes.²⁸ A hazardous waste is a

material that can cause damage to human health or the environment. Heavy metals are considered a hazardous material if they are present in toxic concentrations. Minimizing the amount of the material used will result in the least amount of wastes to be disposed. Accurate engineering, planning and careful use of toxic materials are tools that can help reduce the amounts of waste generated.

The key to waste minimization is to keep wastes containing heavy metals separate from wastes that do not contain metals. One important rule is not to dispose of materials containing metals in drilling pits. For example, once a pit is contaminated all the material becomes non-exempt and must be tested to see if it is classified as a hazardous material.²⁸

6.2 RECYCLING

Recycling materials that contain metals can also reduce environmental impact of the metal because less materials are used and disposed.

6.2.1 DRILLING MUDS: One recycling study found

that treated drilling muds could be successfully reused as drilling mud and the solid residues could be used in cement block and asphalt manufacturing. The excess metal contents were removed using the following processes: pH control, skimming, detoxification, chemical fixation, flocculation, precipitation/co-precipitation, chemical oxidation/reduction, neutralization, emulsion breaking, adsorption, coagulation, and filtration.²⁹

6.2.2 DRILL CUTTINGS: Recycling of drill cuttings will minimize waste, conserves natural resources, and reduces costs associated with drilling waste disposal. A good option for recycling drill cuttings is to reclaim construction grade materials to replace mined gravel.¹⁹ If the cuttings are to be reused they must meet environmental regulations for construction, and the environmental effects will have to be determined on an individual basis.

The initial step to recycle cuttings is to clean the cuttings. One method to clean cuttings is to first

spray the coarser materials with high pressure water to remove clays. The cuttings are then sent across shale shaker screens to separate the large particles from the liquids and smaller particles. The liquids and solids which passed through are collected and agitated to disperse clays and shales. The dispersed material can be sent through a diaphragm pump and then processed across additional screens to separate out usable sand (>279 micrometers). The sand and gravel separated by the screens are then stored for testing and use. The remaining liquids and fines must then be disposed of by approved subsurface disposal techniques.¹⁹

Before use as a construction material, the cuttings must be analyzed for element concentrations. The cuttings themselves must not be a hazard relative to the native gravels and soils. Table 6.1 provides the concentrations of metals from treated cuttings and native soils and gravels from a site in Alaska. The treated cuttings had metal concentrations similar to the metal concentrations of the native soils and gravels.¹⁹

6.2.3 WASTE WATERS: One recycling program used a three phase program to develop and demonstrate an economical method to treat and reuse scrubber blowdown and produced water.²⁹ The program phases were as follows:

(a) Phase 1 - sampling and characterizing wastewaters from exploration and production activities.

(b) Phase 2 - laboratory scale treatment testing.

(c) Phase 3 - field testing full-scale physical and chemical treatment equipment.

Average removal efficiencies for total dissolved solids, chemical oxygen demand, and oil and grease were 95%+. Table 6.2 contains the treated composition of scrubber blowdown, and the percentage of metals removed. Operating costs and water reuse options were also determined. The treatment processes removed much of the toxic material found in the waters, including heavy metals. The recycling recommendations from the study included reusing treated scrubber blowdown as an oxygen scavenger and reusing treated produced waters as boiler feedwater.

6.2.4 OILY SOLIDS: Oily solids are generated from many sources in exploration and production processes, including oil based drilling muds, tank bottom sludges, and oil contaminated soils. All of these wastes have variable quantities of oil and water mixed with the solids. These wastes also contained heavy metals. Cleaning these wastes is difficult because of the wide variety of contaminants. Methods for managing these wastes include recycling and soil remediation or stabilization.

One application for oily wastes is to use them in the maintenance of roads as a road surfacing material instead of asphaltic compounds. The Cold Lake Production Project³⁰ produces an oily sand waste which contains heavy metals. The waste is stored and then selectively removed and prepared for road surfacing. Problems with this method of disposal include environmental hazards from leaching and runoff.

Prior to road application the wastes must be chemically analyzed, the wastes cannot be used on the roads if they do not meet regulatory requirements.

Table 6.3 contains a chemical breakdown of the oily solids that are to be used as road surfacing. The chemical composition of the oil waste roadbed is compared the chemical composition of an asphalt roadway in Table 6.4. The oil wastes in Tables 6.3 and 6.4 are different samples, and are slightly different in composition. The metal concentrations in the oil waste were lower than those of asphalt and for the average soils. The pH of the oil waste and asphalt samples was 7.2, a level at which most of the metals present are not mobile. The results of soil samples from around the roadway have shown no elevations in chemical components, which suggests that the transport of metals away from the roadway from leaching or runoff is not occurring.³⁰

6.3 SUBSTITUTION FOR HAZARDOUS MATERIALS

One method for minimizing the hazardous material used on-site is to replace the hazardous material with a non-hazardous material.²⁸ Several examples of material substitutions are listed in Table 6.5.

6.3.1 PIPE DOPE: One of the most potentially hazardous material is pipe dope. Although only a small amount is needed, techniques normally used in the field often create an excess in the pipe, which is then washed into the reserve pit, contaminating the entire pit. Recently developed pipe dopes contain little to no amounts of heavy metals. One of the new, less toxic, pipe dopes contains alumina-ceramic beads in a lithium grease.¹²

6.3.2 DRILLING FLUIDS: The goal in drilling is to get the best performance at the lowest cost. In today's world of high cost of disposal for hazardous materials, the type of drilling fluid can greatly affect the cost of drilling a well. The most environmentally benign muds include seawater spud, fresh and seawater gels and polymers, and lightly treated lignosulfate muds. These muds are listed with the toxicity for both the liquid and particulate phases in Table 3.5. This list includes water based muds without many toxic additives.⁸ Many new muds are being tested that contain low concentrations of heavy metals in both the base mud and

the additives.

6.4 DISPOSAL AND REMEDIATION

There are four primary methods to restore a site contaminated with metals. These methods include land treatment using indigenous microbes, land farming, thermal treatment, and solidification. Several other methods are being tested for large scale use. The methods can also be used to close and/or restore oil-field waste pits, leaking underground storage tanks (LUST) sites, and general hydrocarbon contamination sites.³¹ The scope of the contamination must be determined for the proper method of remediation to be implemented.

6.4.1 LAND TREATMENT: In the land treatment process, contaminated soil is combined with uncontaminated soil and the resulting soil is left in place. Land treatment is used most often with waste pit closures. Final testing is required to verify that no toxic materials have been left in the waste pit. The best composition for this method is for small

concentrations of metals. Throughout the process the leachate and runoff must be contained.³¹

6.4.2 LAND FARMING: In the process of land farming, temporary treatment cells are erected into which the contaminated and clean soils are mixed with natural or industrial bacteria. Industrial bacteria are more aggressive, and can be developed specifically for a specific waste. Nutrients are also added to speed degradation. Throughout the process, the influent and effluent must be contained to prevent possible groundwater contamination. The cleaned soils must be periodically replaced to prevent a buildup of soluble heavy metals which cannot be immobilized by the soil.^{31,32} The soils can adsorb some of the heavy metals but increasing amounts can overpower both the soils and bacteria.

6.4.3 THERMAL TREATMENT: In thermal treatment the soils are removed from the contaminated area and heat treated. The soil is treated in either a catalytic incinerator, rotary kiln, or fluidized bed incinerator

at about 700 degrees F. The soil is then slightly rehydrated and tested and returned to the excavation. For this method to be successful, it must have adequate combustion of the materials, which requires careful operation and advanced equipment. To meet disposal requirements this method must reduce the oil level to 10 mg/1 kg of dry cuttings and not discharge any other pollutants. The flue gas emissions must also be controlled to meet regulatory requirements.

The residue must then be tested and disposed of properly. For disposal of the solids, an EP or extraction procedure toxicity test is designed to simulate the leaching a waste might undergo if disposed of in an improperly designed solid waste or sanitary landfill. The test uses an aqueous medium whose pH is at or below 5, and the solids are leached for 24 hours. The liquid is then tested for metals. The assumption is that if metals do not leach during the test, they will leach even less if disposed in the ocean or in a normal landfill.^{9, 31}

6.4.4 STABILIZATION AND SOLIDIFICATION:

Stabilization and solidification is a process through which additives are mixed with the contaminated soils to hold contaminants in place, e.g., concrete mix and fly ash. Lime is also used to produce the physical and chemical changes to allow the adsorption of the hydrocarbons and fix the metals as insoluble salts. The higher pH from the added lime is required to prevent the matrix from becoming acidic as water percolates through. This also makes the matrix hydrophobic. The treated soils require long term monitoring to assure no leaching of the contaminants is occurring.^{32,33}

6.4.4.1 STABILIZATION OF HEXAVALENT CHROMIUM

WASTES: The most toxic form of chromium has a chemical valence of (+6) and is called hexavalent chromium, Cr(VI). Hexavalent chrome is commonly found in the raw material for electroplating and as a by-product of other uses. The hexavalent form is very mobile in the environment and an acute and chronic health hazard. To stabilize the chromium wastes, the hexavalent chromium must be transformed to the trivalent form. It is then possible to solidify and stabilize waste through use of

cement like materials such as portland cement or pozzolime.³⁴

Hexavalent chromium can be reduced to less toxic trivalent chrome by putting it in a reducing environment. Reducing agents that can be used include: sodium metabisulfate (NaHSO_3), ferrous sulfate (FeSO_4), and ferrous ammonium sulfate [FAS] ($\text{FeSO}_4(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$).

After reduction to the trivalent form the waste can be stabilized. Stabilization uses amounts of waste and cement in the following proportions: 0.5:1 to 1:1 pozzolime: waste. The residual hexavalent chromium and total chromium concentrations are below 100mg/kg. The resulting waste is stable and will not leach chromium at TCLP standards.³⁴

6.4.4.2 STABILIZATION OF MERCURY WASTES: Mercury is a very toxic and mobile element, but is not very common in petroleum exploration and production wastes. There are several viable Mercury Remediation Technology options:³¹ (1) Thermal recovery technology.

(2) Acid or alkali leaching for low mercury soils

or ones not suitable to thermal recovery. Acid leaching of incineration residues is required.

- (3) Immobilization/Stabilization processes which is the best available technology for radioactive mercury.
- (4) Extraction with complexing agents
- (5) Ion exchange resins
- (6) Electroreclamation by electrokinetic transport

6.4.5 IN-SITU VITRIFICATION: In-situ vitrification converts contaminated soil into glass and crystalline product by melting it with electrical energy. The heavy metals are rendered immobile by being incorporated into the glass and crystalline structure. Table 6.6 lists the concentrations of metals present in the leachate from the TCLP test before and after the vitrification process from one study. This procedure is only in the research stage and does not appear to have large scale applications in the petroleum industry. But for small contained spills with a high metals content it may have some merit.³⁵

6.4.6 BIOREMEDIATION: An important application for bioremediation is in the reduction of oil contents on drill cuttings, especially from oil based muds. The drilling fluids contain heavy metals which are attached to the cuttings. One option for cleaning the oils and metals from the cutting is in-situ bacterial degradation. The presence of arsenic, barium, cadmium, chromium, lead, mercury, nickel, selenium, silver, and vanadium on the cuttings can adversely effect the microbial populations.

Metals cannot be destroyed, but they can be recovered or made less toxic by some microorganisms. These microorganisms use metals in their enzyme systems. The microbes oxidize, reduce, methylate, demethylate or otherwise transform the metals so that the solubility, sorption, and volatility in soil is changed. The rate of heavy metal uptake by tolerant microorganisms is metabolism dependent. The metals that are not used by the microorganism may be precipitated intercellularly and stored.

The soil can be manipulated to increase the transformation of metals in the soil. The process

requires that the pH, organic matter content, and temperature be increased, while the oxygen content is decreased. The second step is to increase the soil moisture content and increase the oxygen content. The final step is to raise the pH of the system to a point where the remaining metals will remain adsorbed to the soil. This method has potential for soil decontamination, but requires a two to three year period for the process to work.^{25,36,37,38}

**TABLE 6.1: SUMMARY OF ELEMENTAL CONCENTRATIONS IN
NATIVE SOILS (Alaskan North Slope) AND PROCESSED
DRILL CUTTINGS (mg/kg dry)^{1a}**

ELEMENT	MEAN SOILS	MEAN CUTTINGS
Aluminum	7050.0	3839.0
Arsenic	1.83	7.31
Barium	397.0	775.1
Boron	29.4	29.3
Cadmium	0.153	0.30
Calcium	46700.	2975
Chromium	11	8.418
Copper	14	18.2
Iron	19600	8436
Lead	4.24	30.16
Magnesium	3440	2081
Manganese	484	148.77
Mercury	0.268	0.295
Nickel	21.3	15.21
Potassium	699	663.0
Selenium	0.267	---
Silicon	1640	1254.0
Silver	0.26	0.473
Sodium	529	1048.5
Strontium	93.4	59.2
Vanadium	29.9	23.05
Zinc	74.6	79.21
Chloride	1250	---
Sulfate	396	---

**TABLE 6.2: RESULTS OF FIELD TREATMENT OF
SCRUBBER BLOWDOWN^{2a} (ppm)**

COMPONENT	INFLUENT	EFFLUENT	FILTER CAKE	%REMOVAL
CHROMIUM	0.16	0.08	48.7	50.00
COPPER	0.18	0.04	9.73	77.78
IRON	7.56	0.34	2063.0	95.50
NICKEL	8.84	0.65	1739	92.65
VANADIUM	36.75	2.45	1635	93.33
pH	6.8	6.6		

NOTE: NO ATTEMPT TO REMOVE SOLUBLE METALS,
EVALUATING ONLY SUSPENDED SOLIDS AND FILTER CAKE

TABLE 6.3: CHEMICAL CHARACTERIZATION OF OILY SAND WASTE²⁹

COMPONENT	CONCENTRATION
PHYSICAL PROPERTIES	%
Oil	13.0
Liquid	7.5
Solid	79.5
INORGANIC CHEMICALS	(ppm)
Boron	0.01
Cadmium	0.001
Chromium	0.066
Lead	0.05
Mercury	0.0001
Manganese	0.03
Nickel	0.008
Vanadium	0.05
Chlorides	780.0
pH	6.9

**TABLE 6.4: COMPARISON OF COLD LAKE OIL WASTE ROADWAY
AND ASPHALT ROADWAY AND MEAN SOIL CONCENTRATIONS^{2, 29}**

COMPONENT	OIL WASTE (PPM)	ASPHALT (PPM)	MEAN SOIL
Arsenic	0.04	0.10	0.1-40
Barium	0.55	2.80	
Boron	0.1	0.38	
Cadmium	0.001	0.01	0.01-2
Chromium	0.6	0.16	5-1500
Copper	0.06	0.36	2-250
Lead	0.057	0.63	2-300
Mercury	0.0001	0.0001	0.01-0.5
Selenium	0.0017	0.0002	0.01-2
Zinc	0.14	0.99	1-900
pH	7.2	7.2	6.5

TABLE 6.5: SUBSTITUTES FOR TOXIC MATERIALS^{1 2}

HAZARDOUS ITEMS	ENVIRONMENTALLY SAFE REPLACEMENTS
Pipe Dope Compounds: Lead, Zinc, Copper, Cadmium	Nonhazardous Lithium-Based Grease with Microsphere Ceramic Balls
Oils and Greases: Aromatics, Sulfur Leaves Oil Sheen	White Oils Manufactured From Highly Refined Mineral Oils Approved for Use in the Food Industry
Cleaning Solvents: Varsol, Freon, MEK,	Citrus-Based Solvents, High Pressure Hot Water
Phosphate Soaps	Jet Washers, Closed Loop Recycling

TABLE 6.6: TABLE OF METAL CONCENTRATIONS BEFORE AND AFTER VITRIFICATION PROCESS.³⁴

CONTAMINANT	INITIAL CONCENTRATION	TCLP CONCENTRATION	ALLOWABLE CONC.
Arsenic	4400	<5	5
Barium	4400	<1	100
Cadmium	4400	<1	1
Chromium	270 - 4400	<0.2 - 2.7	5
Silver	4400	<0.1	5
Lead	50	<0.1	5
Mercury	46	<0.0001	0.2

(TCLP) TOXIC CHARACTERISTICS LEACH PROCEDURE TESTS

CHAPTER 7. CONCLUSIONS

Petroleum drilling and production operations can introduce heavy metals into the environment. Heavy metals are of concern because they can impact the health of living organisms that they contact.

The amount of heavy metals released by the petroleum industry and its percentage relative to other sources of heavy metals are summarized in Tables 7.1, and 7.2. From these tables it can be seen that the petroleum industry contributes only a small fraction of the heavy metals to the environment compared to both natural sources and other industrial sources of heavy metals.

The bioavailability of the metals introduced into the environment by the petroleum industry are very low. The bioavailability is low because the metals have a very low solubility at pH's normally present in the environment. The preferential sorption of free metal ions to sediment particles also reduces the bioavailability.

Recycling and proper waste treatment and disposal are viable options for reducing the environmental

impacts from heavy metals. Methods for treating contaminated soils which have been successfully tested in the field include land farming, land treatment, stabilization and solidification, and bioremediation. Treated produced water and drilling fluids have been recycled as feedwater and drilling fluid. Drill cuttings and oily sand wastes have been used as construction material for roads.

The relatively small amounts of metals introduced into the environment by the petroleum industry, the low bioavailability of these metals, and the availability of effective waste treatment methods, translates to a minimal impact from metals on the environment by drilling and production operations. Heavy metals from the production of petroleum, properly handled, are not a threat the environment.

**TABLE 7.1: AMOUNT OF HEAVY METALS RELEASED TO THE ENVIRONMENT
7,8,13,14 (10⁶ gm/year)**

SAMPLE	U.S. PRODUCED WATER	U.S. DRILLING WASTES	NATURAL AIR EMISSIONS	INDUSTRIAL PARTICULATES	FOSSIL FUEL COMBUSTION
Ag	0.41	NR	0.60	40.0	10.0
Al	41.33	NR	489258.4	40000.0	32000.0
Cd	0.21	<0.1	2.90	40.0	15.0
Co	12.40	NR	70.04	24.0	20.0
Cr	0.41	1.76	584.01	650.0	290.0
Cu	0.02	6.72	193.01	2200.0	430.0
Fe	1735.86	NR	277753.7	75000.0	32000.0
Mn	103.32	NR	6052.1	3000.0	160.0
Ni	8.70	4.34	283.01	600.0	380.0
Pb	2.07	4.86	58.71	16000.0	4300.0
Sn	12.40	NR	52.41	400.0	30.0
V	1.65	17.04	650.05	1000.0	1100.0
Zn	6.2	41.83	358.14	7000.0	1400.0

NR is for values that were not reported.

TABLE 7.2: PERCENTAGE OF HEAVY METALS RELEASED TO THE ENVIRONMENT FROM THE PETROLEUM INDUSTRY RELATIVE TO OTHER SOURCES^{7, 8, 13, 14}
(10⁸ gm/year)

SAMPLE	% PETROLEUM INDUSTRY	% NATURAL SOURCES	% INDUSTRIAL PARTICULATES	% FOSSIL FUEL
Silver	0.8	1.2	78.4	19.6
Aluminum	0.007	87.2	7.1	5.7
Cadmium	0.36	5.0	68.7	25.8
Cobalt	9.8	55.4	18.9	15.8
Chromium	0.03	38.27	42.6	19.0
Copper	2.4	6.8	77.7	15.2
Iron	0.45	0.45	77.9	8.2
Manganese	1.1	65.0	32.2	1.7
Nickel	1.02	22.2	47.0	29.7
Lead	0.03	0.3	78.6	21.1
Tin	2.5	10.6	80.8	6.1
Vanadium	0.68	23.5	36.1	41.1
Zinc	0.55	4.1	79.5	15.9

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VITA

Katherine Daniels Ware was born in Arlington, Virginia, on March 12, 1963, the daughter of Dannelle Salmen and Mark J. Daniels. After completing her work at Highland High School, Albuquerque, New Mexico, in 1981, she enter the Colorado School of Mines, in Golden, Colorado. She received the degree of Bachelor of Science from the Colorado School of Mines in May, 1985. She was commissioned as a United States Navy Civil Engineer Corp officer in September, 1986, and is continuing on active duty. She entered the Graduate School of the University of Texas in August, 1991.

Permanent address: 2828 Espanola Dr. N.E.
Albuquerque, New Mexico 87110

This report was typed by the author.